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Structural phase transitions in elpasolite-like fluorides comprising rare earth elements – Raman scattering study

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Crystals of elpasolite-like fluorides A_2BReF_6 (space group of the high symmetry phase is $Fm3m$, $Z = 4$) belong to a wide family of perovskites studied intensively for decades. Such interest to fluorides is due to numerous phases and phase transitions observed in this family [1] as well as their perspective applications: normally their transparency window is much wider than that of more traditional oxides while their spectral properties may be varied easily by partial or complete substitution of rare earth ions Re^{3+}.

Most of phase transitions in perovskite-like crystals are induced by displacements of a central ion in ReX_6 octahedrons or by rotations of these octahedrons due to soft phonon modes condensations. Such condensations have been found many times in chlorine-, bromine- and oxygen-containing elpasolites (see, e.g., [2-4]), but only occasionally in fluorides [5]. Here we present Raman scattering investigations of lattice dynamics in several fluorides with elpasolite structures.

Samples have been synthesized from melt as described in [5,6] and cut along crystallographic axes of the cubic phase. Raman spectra have been obtained with Jobin Yvon – Horiba T-64000 spectrometer and Ar^+ laser (514.5 nm, 50 mW), CCD detection with liquid nitrogen cooling, 600 s accumulation time. To interpret results empirical simulations with LADY software and first principle VASP were performed.

High temperature phase of all studied crystals is cubic, and no indications of lattice disorder were found; observed temperature dependences of phonon damping correspond to normal anharmonic decay. Cooling down and shortening of interionic distances result in lowering of the low frequency phonon dispersive branch in Γ–X direction and instability of the cubic phase. Eigenvectors of this branch in the cubic phase correspond to rotations of ReX_6 octahedrons, while in the lower temperature monoclinic phase they mix with cations displacements. In crystals with relatively lightweight rare earth ions (Sc, In) temperature dependences of higher frequency phonons correspond to phase transitions of the first order, closer to the second one, while in crystals with heavier ions (Ho, Dy) this intermodal interaction becomes stronger and their cubic phase transforms into the monoclinic one directly by the first order phase transition. In contrast to "classical" soft mode restorations we observed in these crystals strong interactions of main and secondary order parameters fluctuations that reduce the range of the intermediate tetragonal phase for heavier rare earth ions.

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